Clay-based Oilfield Fluids

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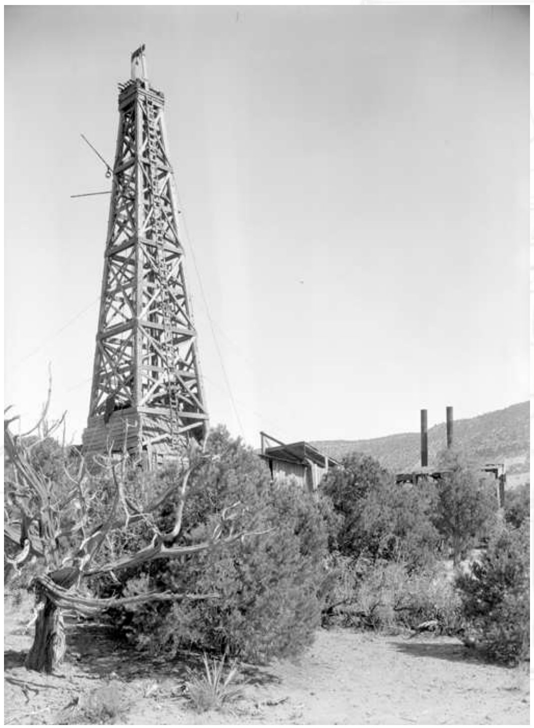
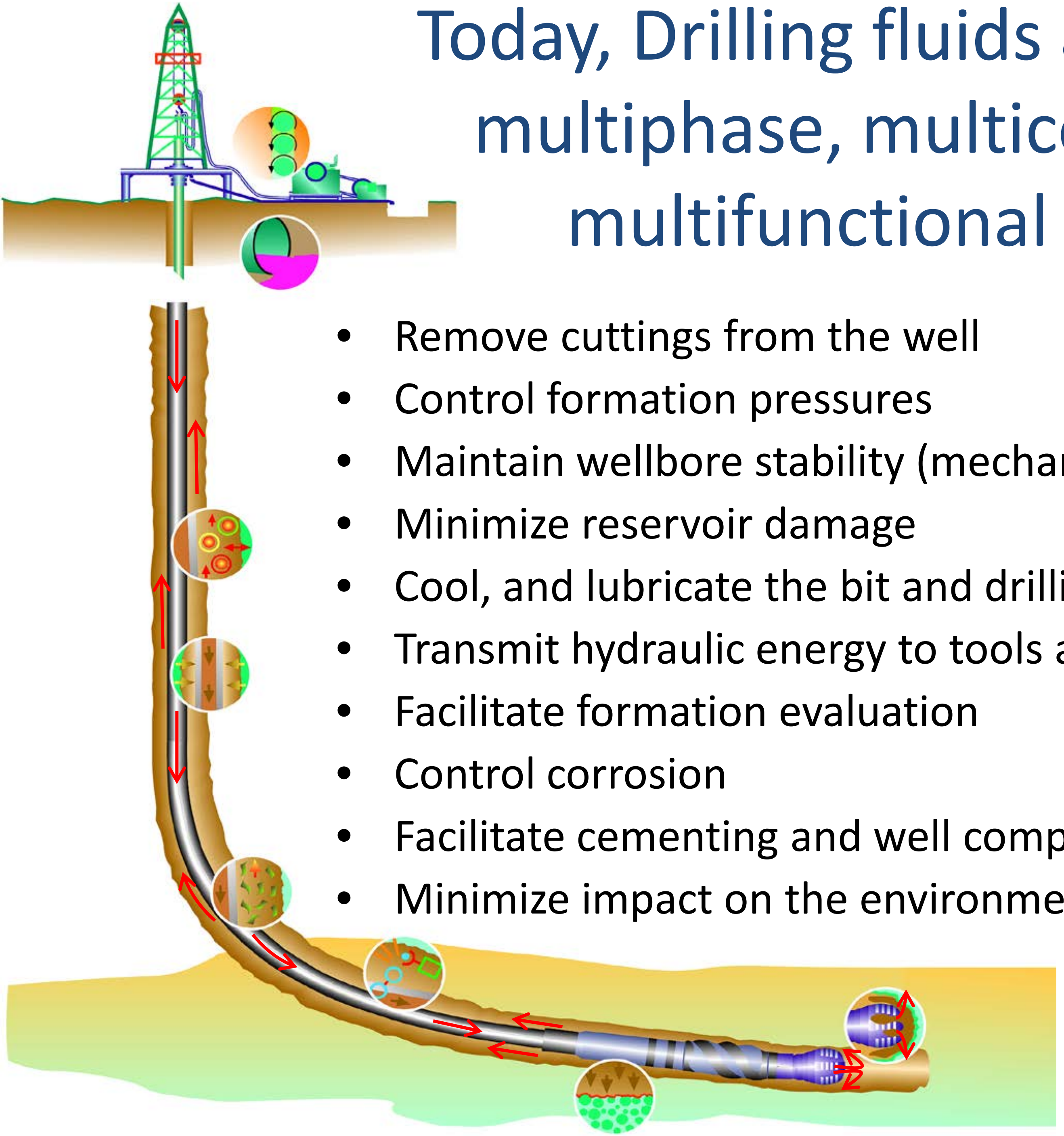
Drilling Mud: a 20th century innovation

October 1900: Spindletop, Texas



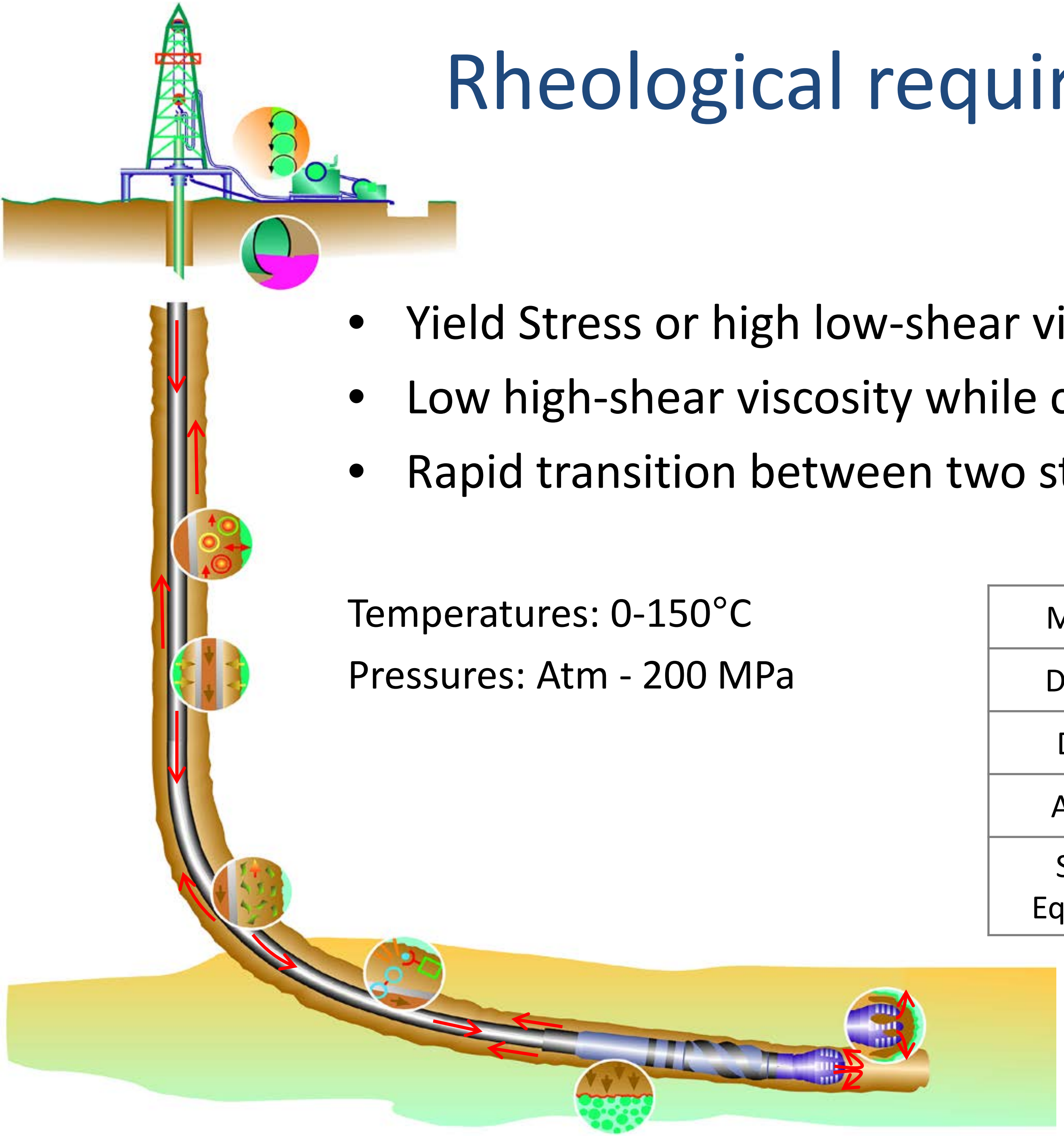
Drillers noticed drilling improved after cattle ‘muddied’ the creek they were using as a water supply

Today, Drilling fluids are complex, multiphase, multicomponent, multifunctional systems



- Remove cuttings from the well
- Control formation pressures
- Maintain wellbore stability (mechanical & chemical)
- Minimize reservoir damage
- Cool, and lubricate the bit and drilling assembly
- Transmit hydraulic energy to tools and bit
- Facilitate formation evaluation
- Control corrosion
- Facilitate cementing and well completion
- Minimize impact on the environment

Rheological requirements



- Yield Stress or high low-shear viscosity at rest
- Low high-shear viscosity while circulating
- Rapid transition between two states

Temperatures: 0-150°C

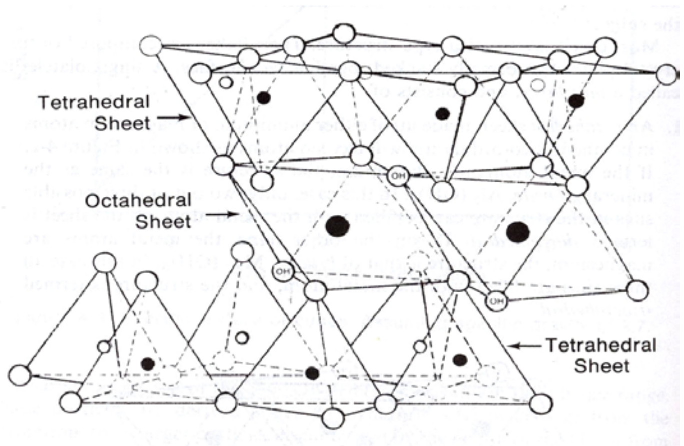
Pressures: Atm - 200 MPa

	Shear rate / s^{-1}
Mud pits	< 1 - 5
Drill pipe	100 - 10,000
Drill bit	10,000 -100,000
Annulus	1 - 200
Surface Equipment	100-1000

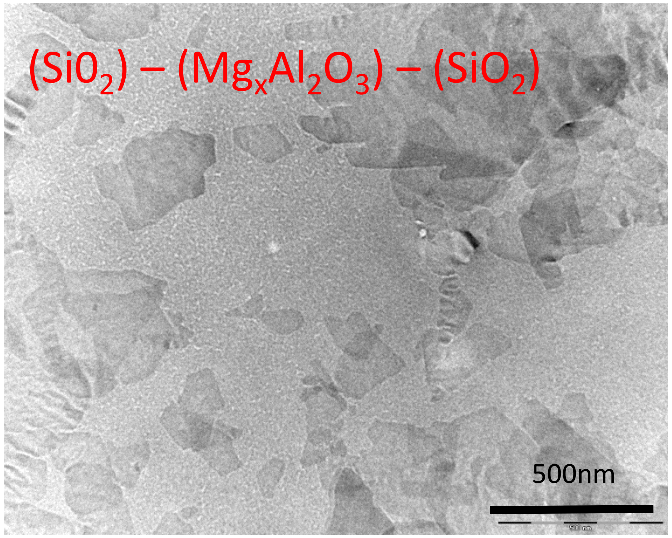
Clay Viscosifiers

Anisotropic mineral particles with high surface charge (face charge –ve, pH dependent edge charge -/o/+)

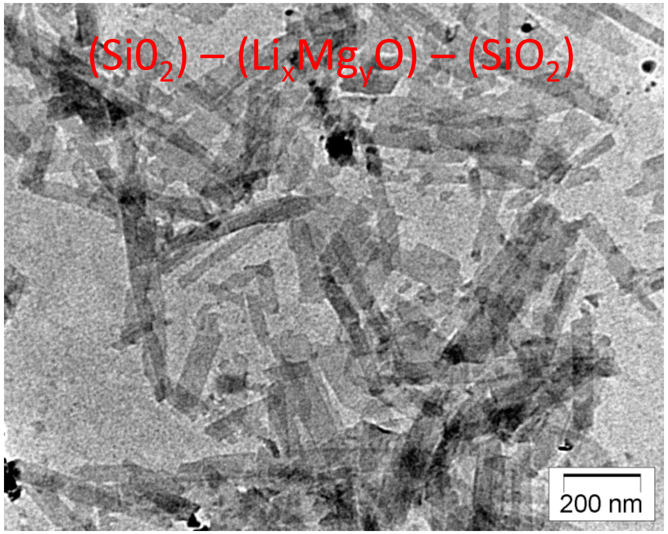
- Strongly gelling fluids at low concentrations
- Good suspending properties at rest / low shear
- Highly shear thinning



Montmorillonite



Hectorite

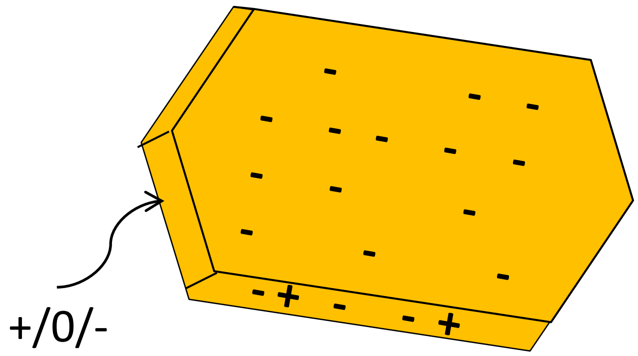


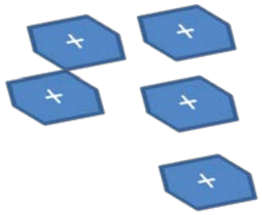
MMH (MMO) Systems

Hydrotalcites, layered double hydroxides

$Mg_xAl_y(OH)_z$ "cationic clay"

- Industrial catalyst support
- Very small hexagonal plates (pure form, industrial material poorly x-talised)
- ~1/10th size montmorillonite





-ve clay +mmh = flocculated system

- Addition of small amount (1:10) MMH to clay system
- High yield stress
- Faster gel time due to smaller particles (faster rotation)
- Very salt, pH & additive sensitive

Model Clay –Extender systems

Base clay (-ve)

- Montmorillonite, SWy-2 — plates ~250 x 250 x 1 nm
- Hectorite, SHCa-1, — laths ~ 300 x 40 x 6 nm

Second colloid (+ve)

- Boehmite — rods ~200 x 10 x10 nm
- Gibbsite — plates ~ 80 x 80 x 6 nm
- Ludox Silica CL — spheres ~ 17 nm

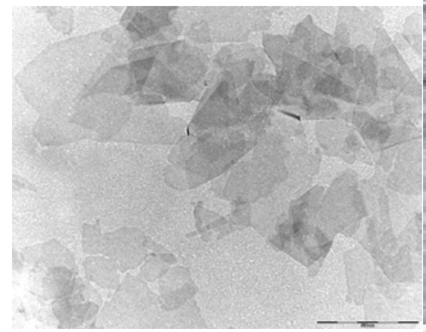
Second colloid (-ve)

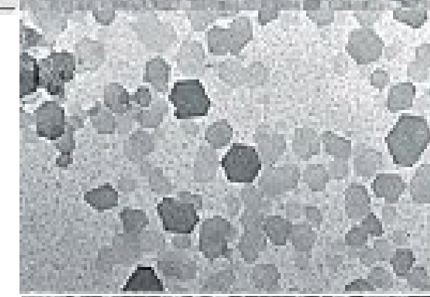
- Laponite — plates ~ 30 x 30 x 6 nm
- Ludox Silica AS40 — spheres ~ 12 nm
- Ludox Silica TMA — spheres ~ 24 nm

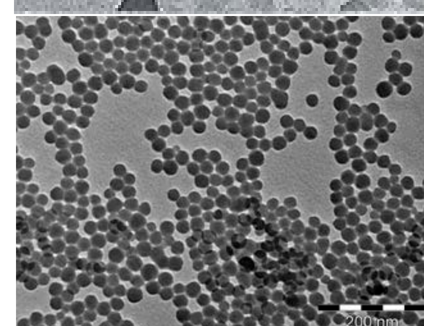
~2.5% wt suspensions in water, mixed 10:1

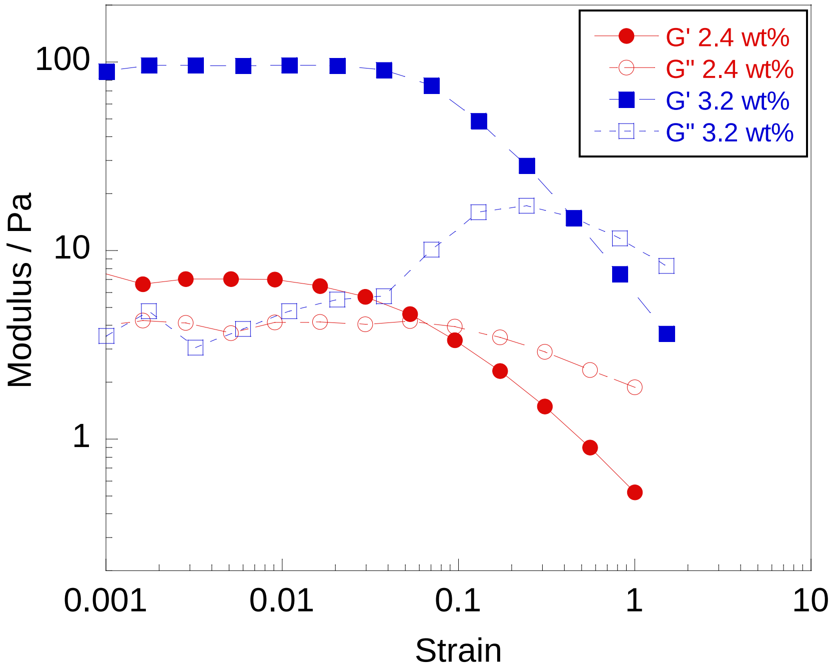
Low salinity, pH > 7

Systematic variation of shape and sign of charge of second colloid









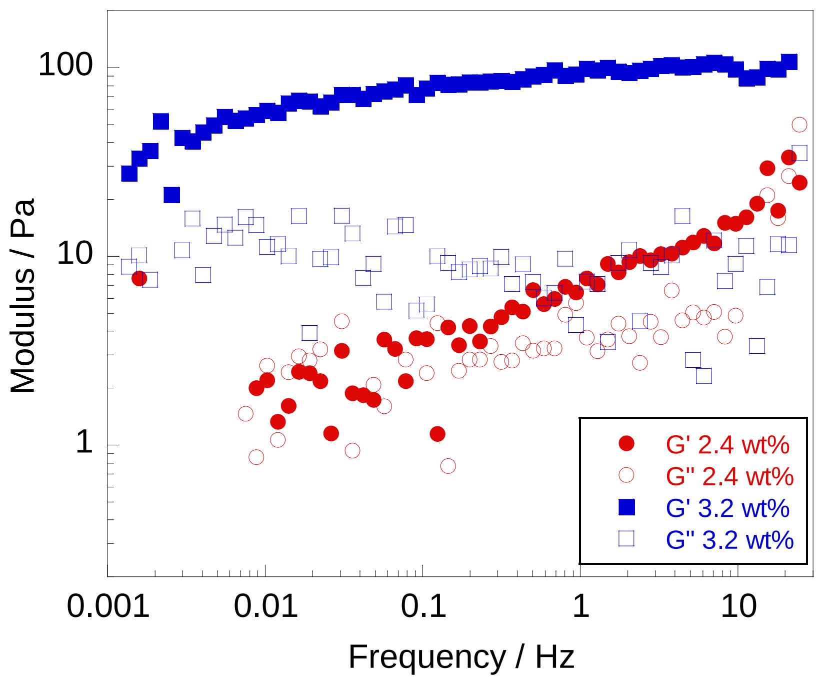
Montmorillonite Oscillation

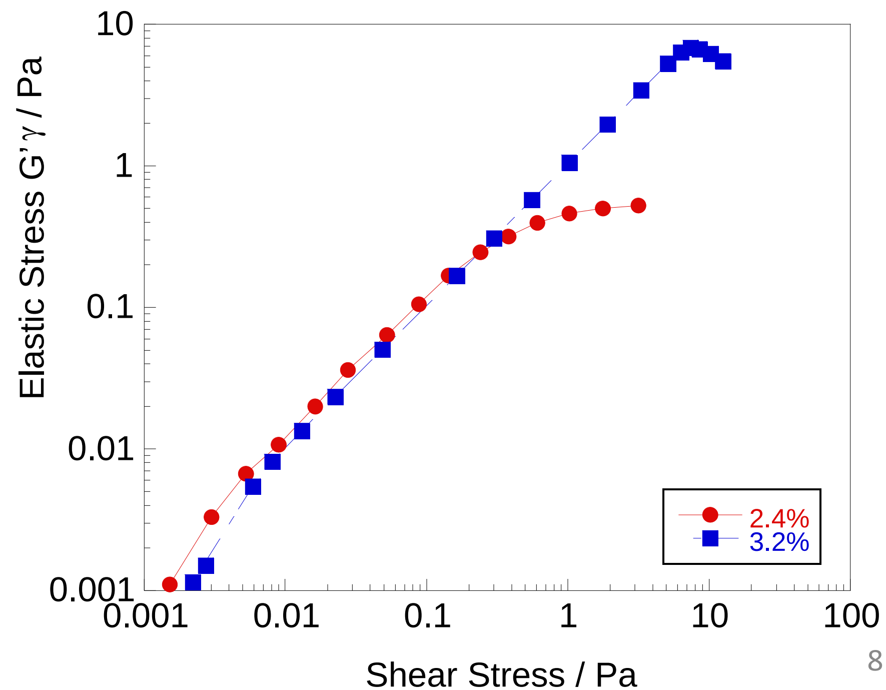
2.4 wt%: still some liquid-like character, G'(freq) ~G" , c* ~2.5

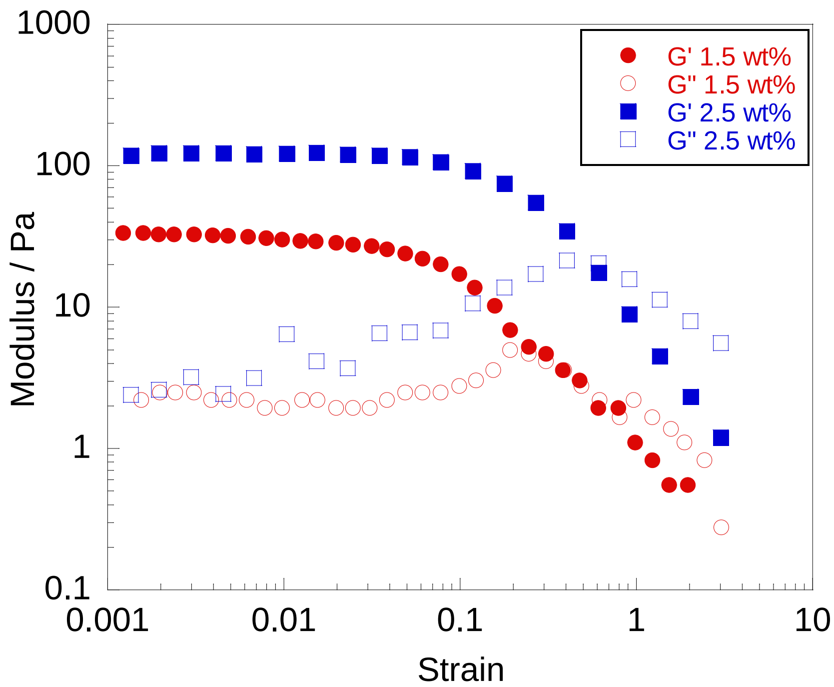
Classic Particle Gel Behaviour @ 3.2 wt% : G' > G"

2.4%: τ_y ~3 Pa, $\gamma_y = 0.06$

3.2%: $\tau_y = 8$ Pa, $\gamma_y = 0.4$





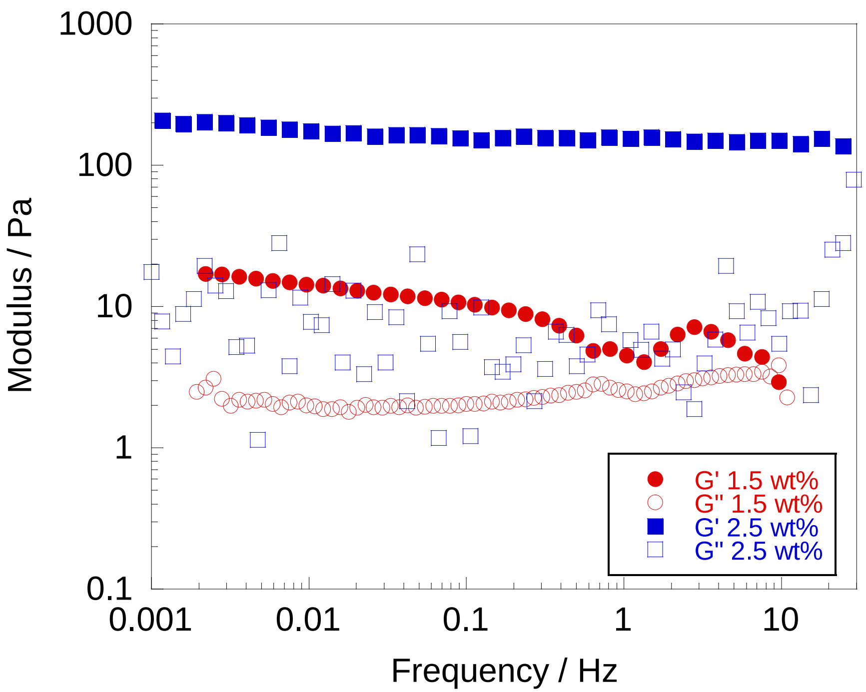


Hectorite Oscillation

c* ~ 1.5 wt%

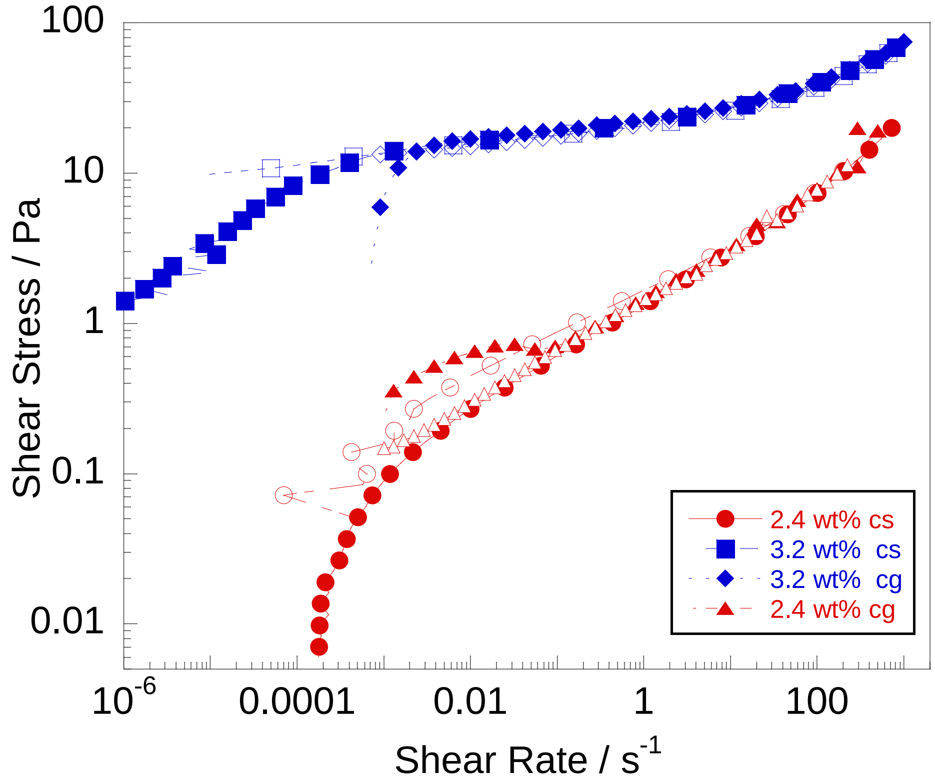
1.5 wt%: τ_y = 1.4 Pa, γ_y ~0.3

2.4 wt% : τ_y = 13 Pa, γ_y ~0.4



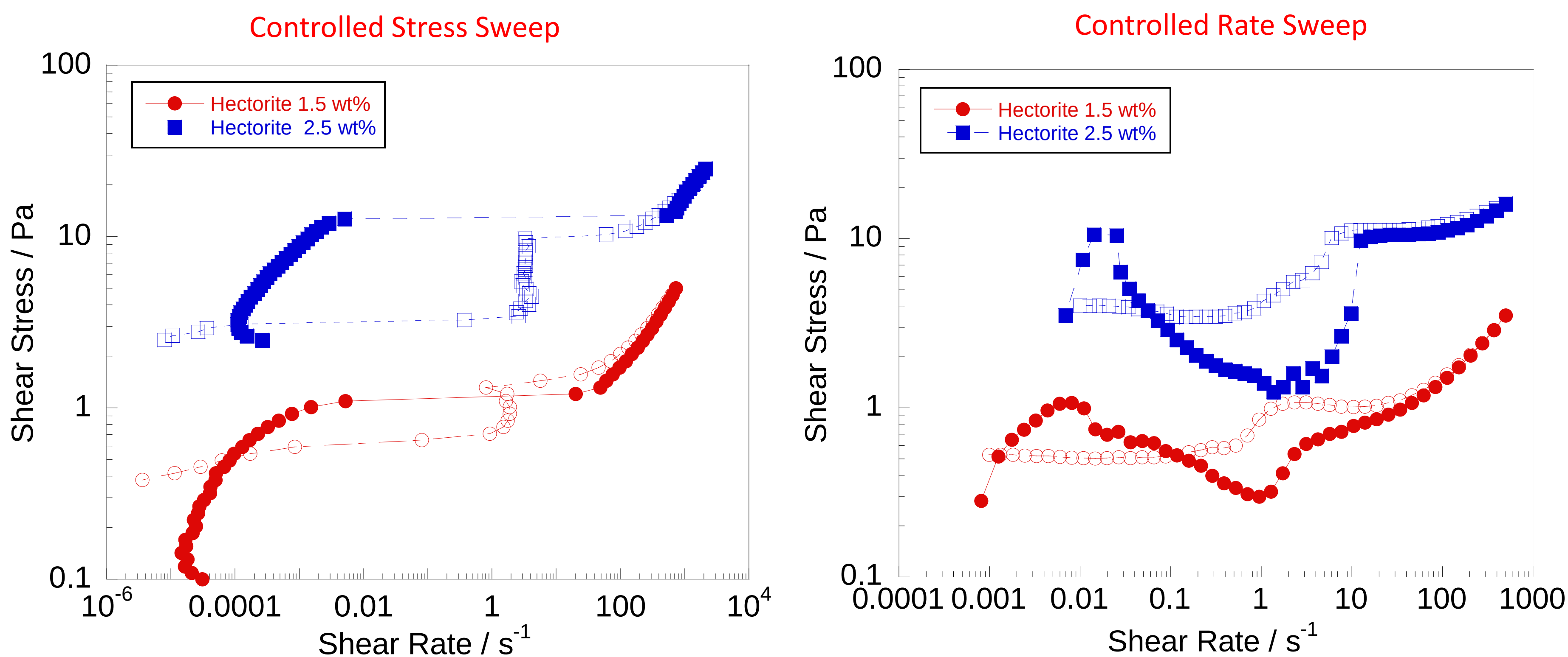
Broadly similar to montmorillonite but stronger gels at comparable c/c*

Montmorillonite - Viscometry



Simple rheograms: little difference between controlled stress (cs) and controlled shear rate (cg) modes, little thixotropy / rheopectry

Hectorite - Viscometry



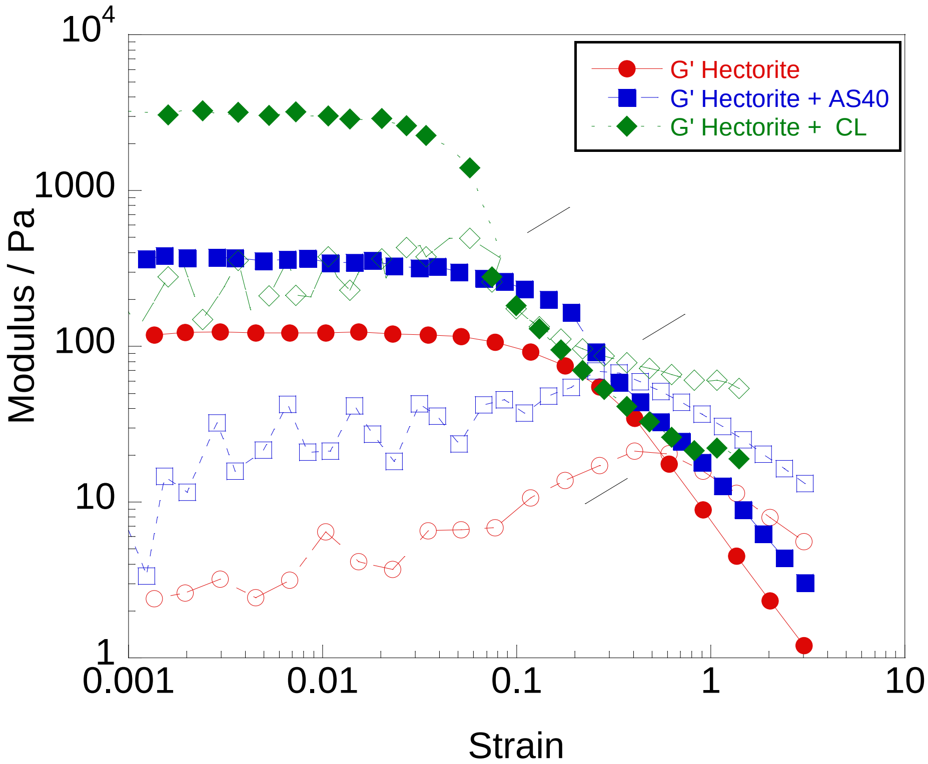
- More complex, structured rheograms, very different in controlled stress / shear rate modes

Particle Mixtures

- Hectorite laths + anionic or cationic spheres
- Montmorillonite plates + anionic or cationic spheres
  - Ludox AS40, TMA, CL

Hectorite + Ludox Silica - Oscillation

c > c*



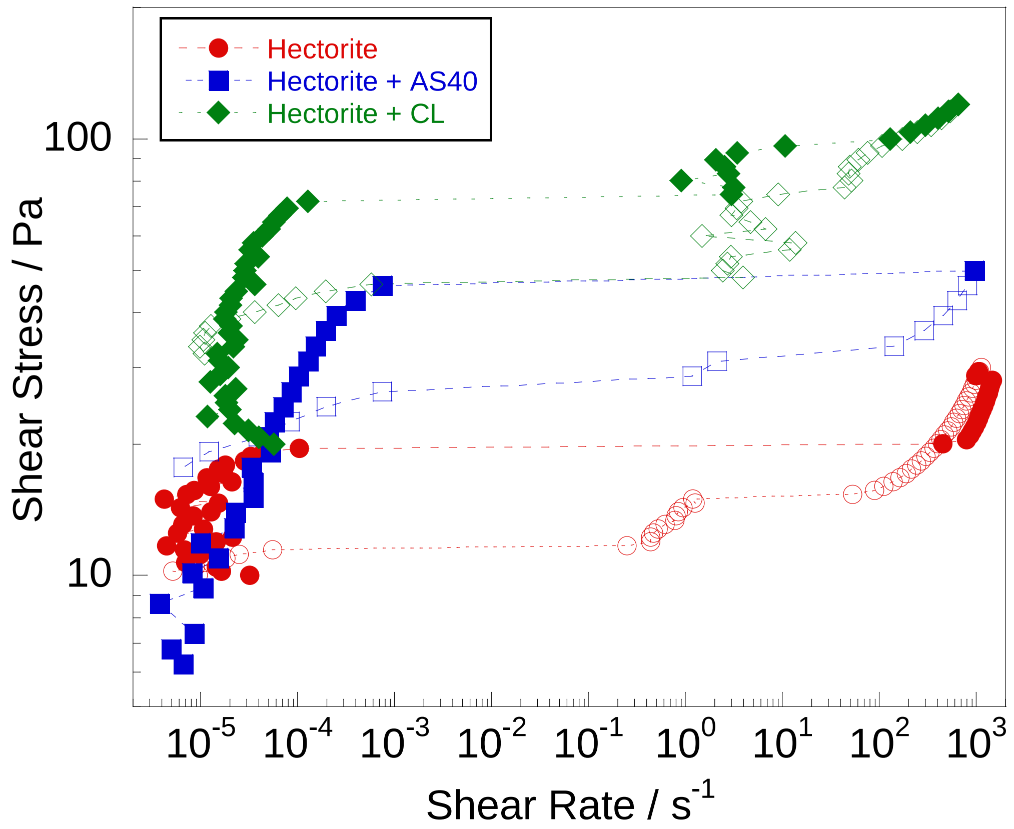
Hectorite: τ_y = 13 Pa, γ_y = 0.4

Hectorite + AS40: τ_y = 30 Pa, γ_y = 0.3

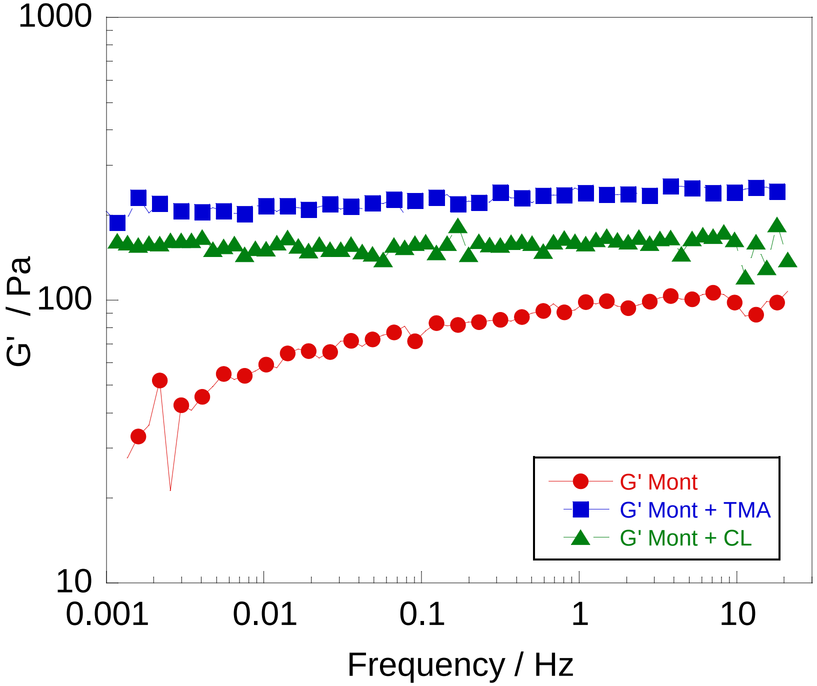
Hectorite + CL: τ_y = 80 Pa, γ_y = 0.08

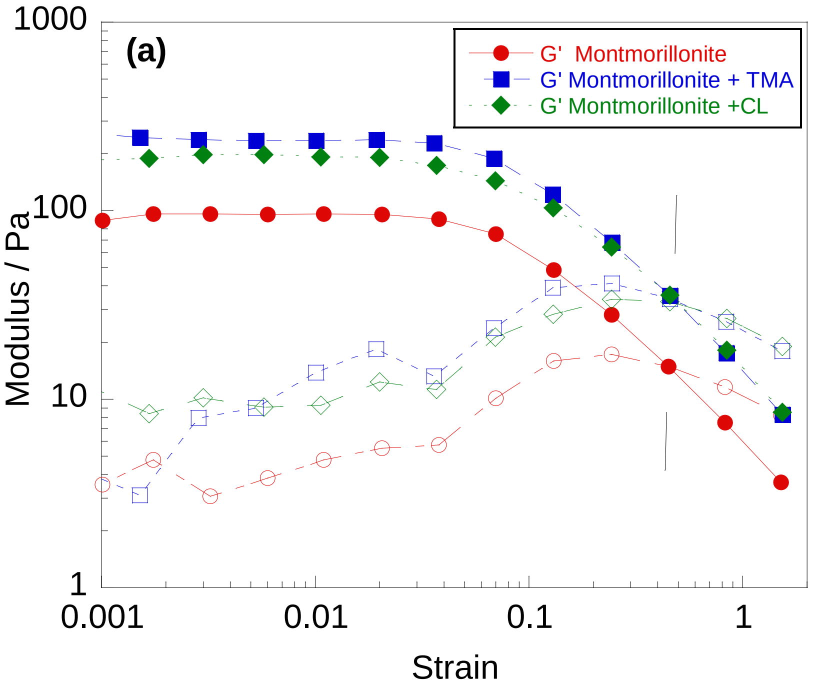
Hectorite + Ludox Silica - Viscometry

c > c*



Complexity of rheogram retained in mixtures,
enhancement of rheology with cationic and anionic silicas





Montmorillonite + Ludox Silica - Oscillation

3.2 wt%, c > c*

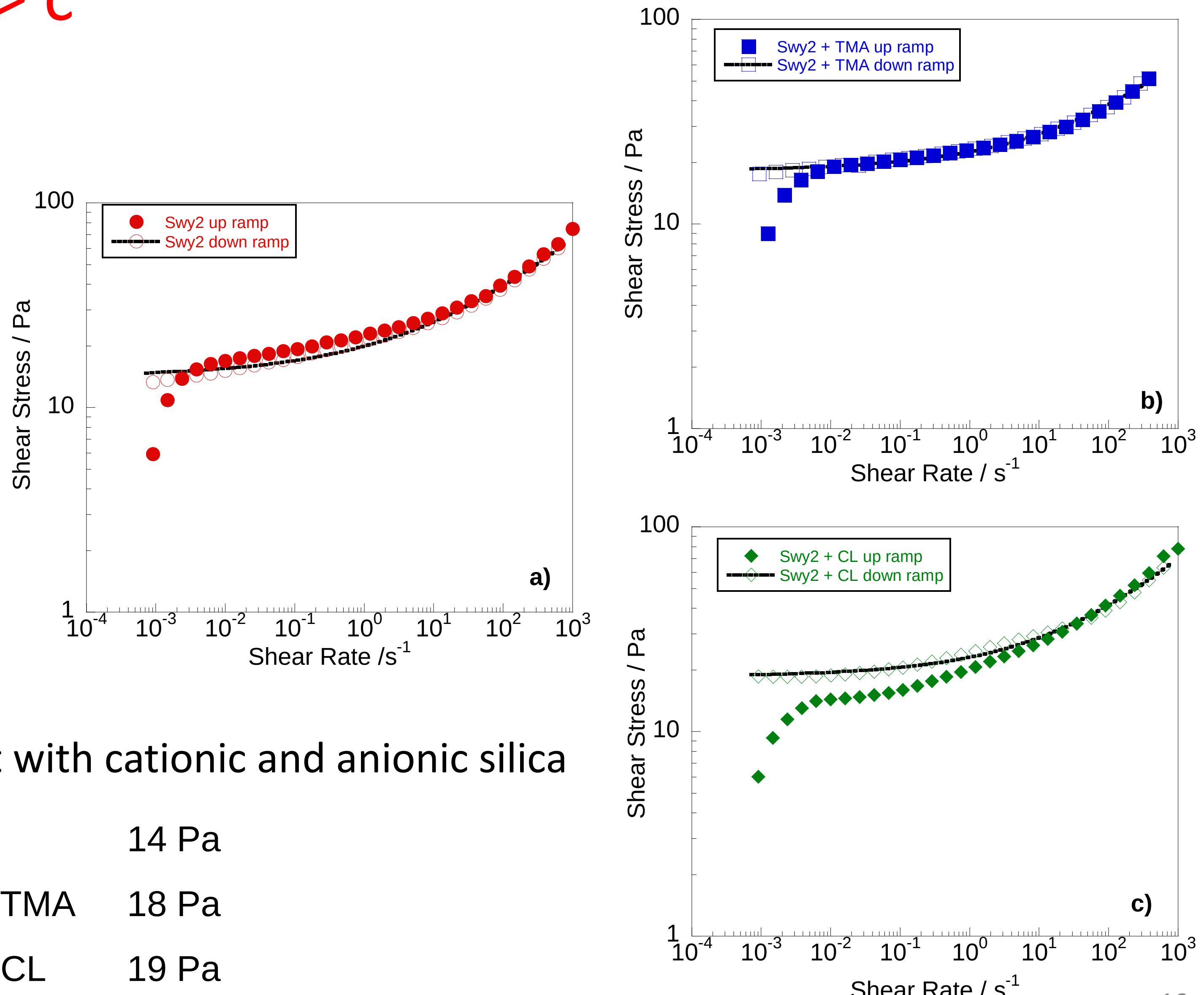
Montmorillonite: τ_y ~8 Pa, γ_y = 0.45

+ TMA: τ_y ~13 Pa, γ_y = 0.45

+CL: τ_y ~13 Pa, γ_y = 0.45

Montmorillonite + Ludox Silica - Viscometry

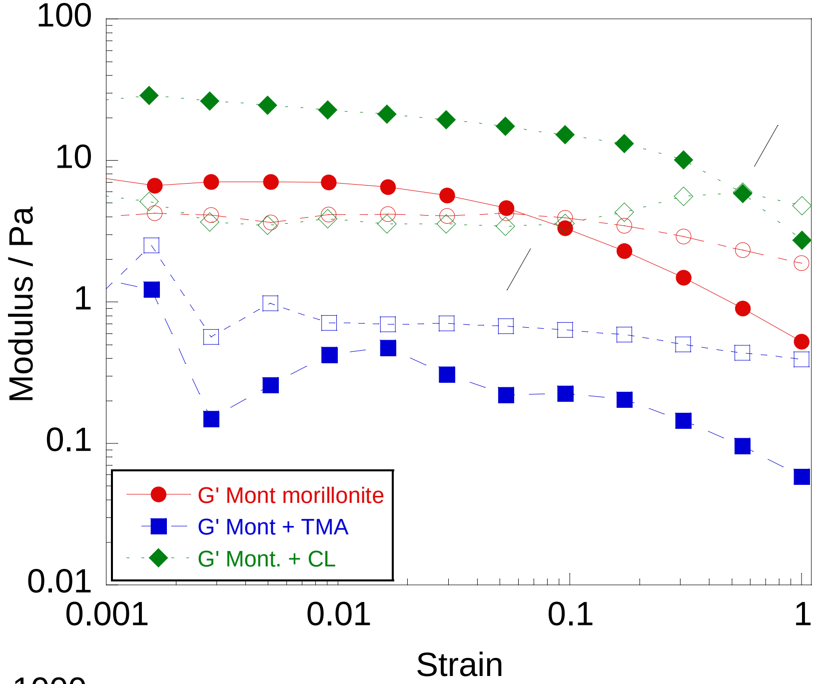
3.2 wt% c > c*

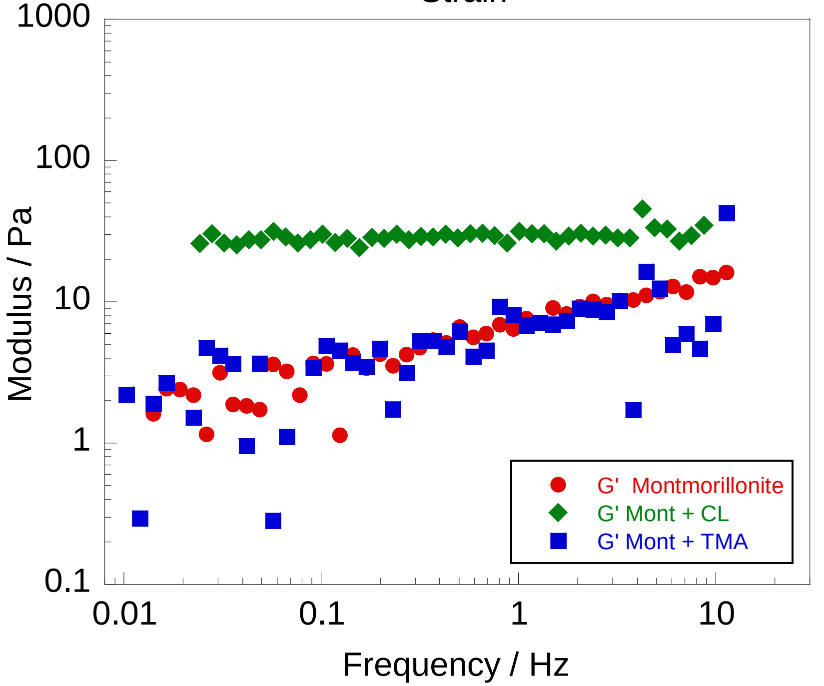


Small enhancement with cationic and anionic silica

Montmorillonite	14 Pa
Montmorillonite + TMA	18 Pa
Montmorillonite + CL	19 Pa

Montmorillonite + Ludox Silica $c \leq c^*$ Oscillation



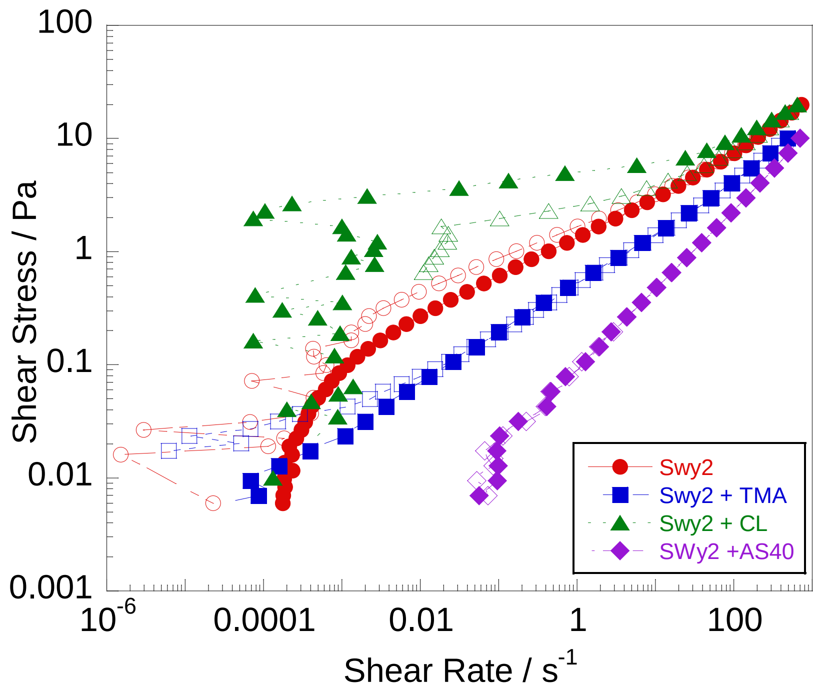


2.4 wt%, $c \leq c^*$

Montmorillonite:	τ_y ~3 Pa, $\gamma_y = 0.06$
+ TMA:	G" > G'
+AS40 :	Too low to measure
+CL:	τ_y ~3 Pa, $\gamma_y = 0.56$

Montmorillonite + Ludox Silica - Viscometry

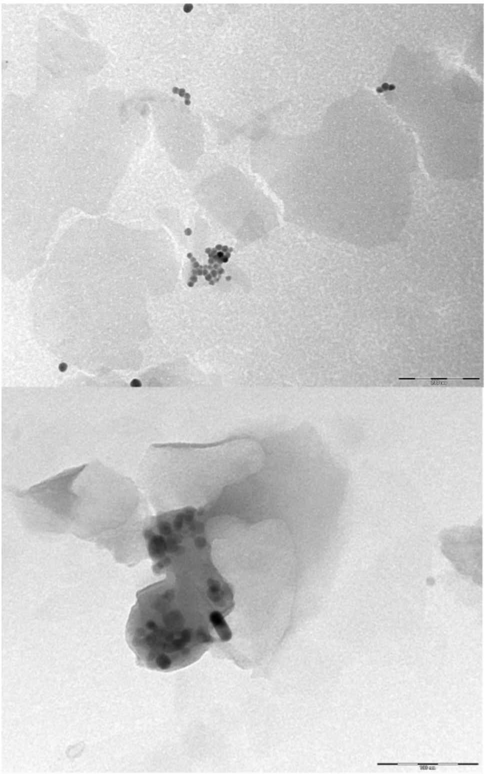
2.4 wt% c ≤ c*



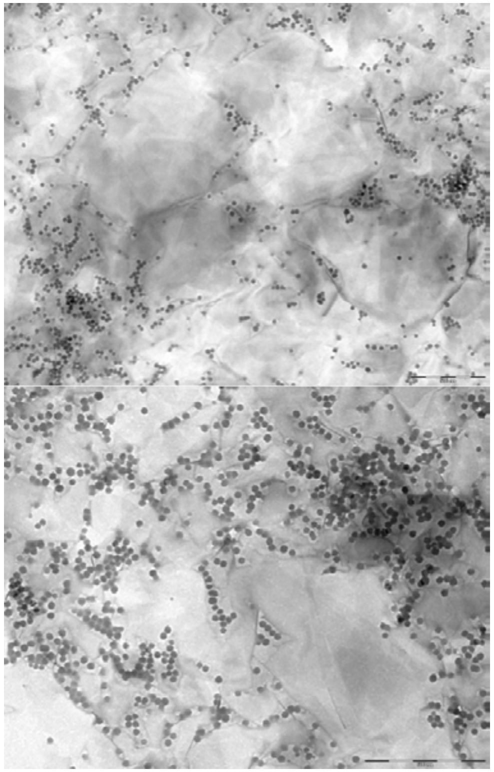
enhancement of rheology with cationic silica
Reduction with anionic silicas

Different Structural Domains with different Silicas

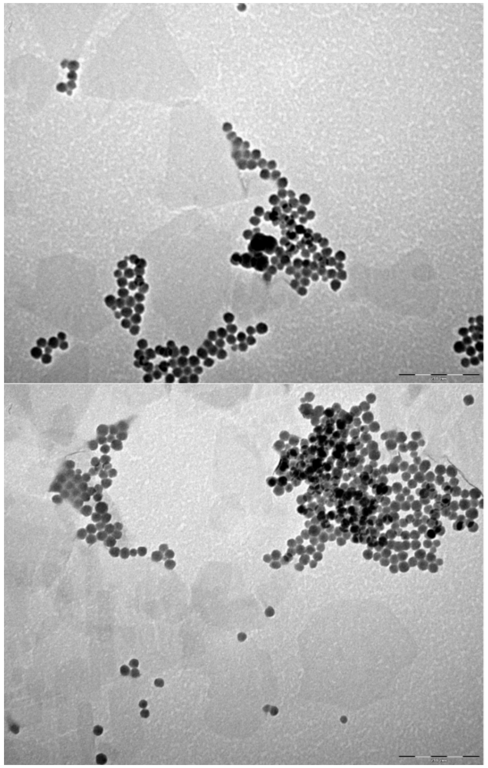
Montmorillonite + CL



Montmorillonite + AS40



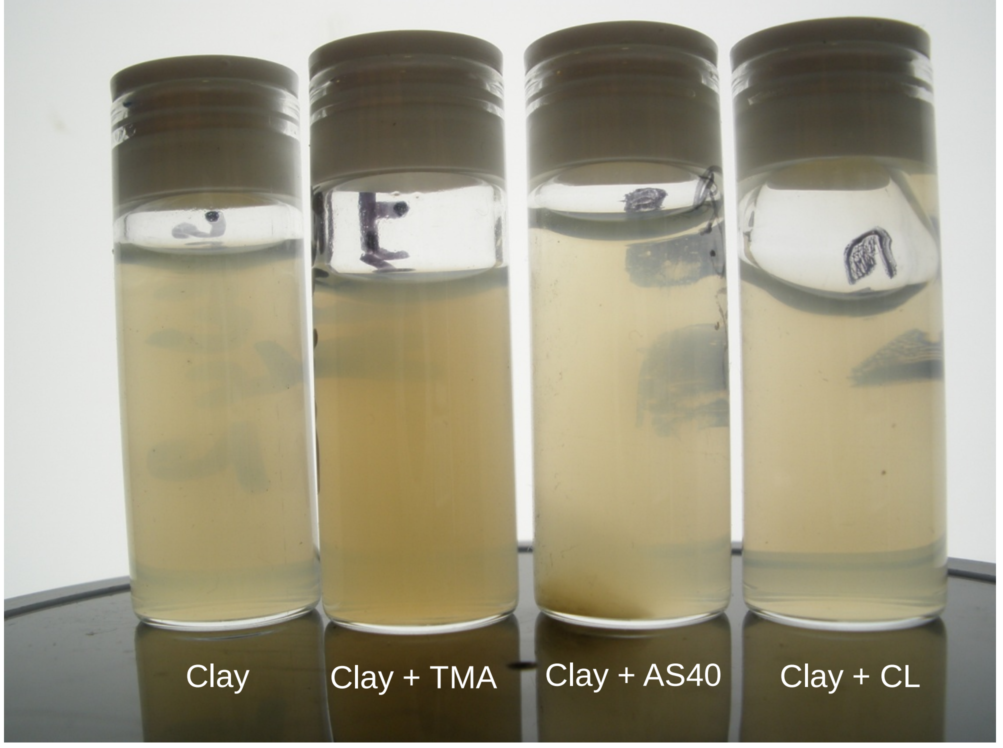
Montmorillonite + TMA



Diluted suspensions for TEM study ~0.01 wt%

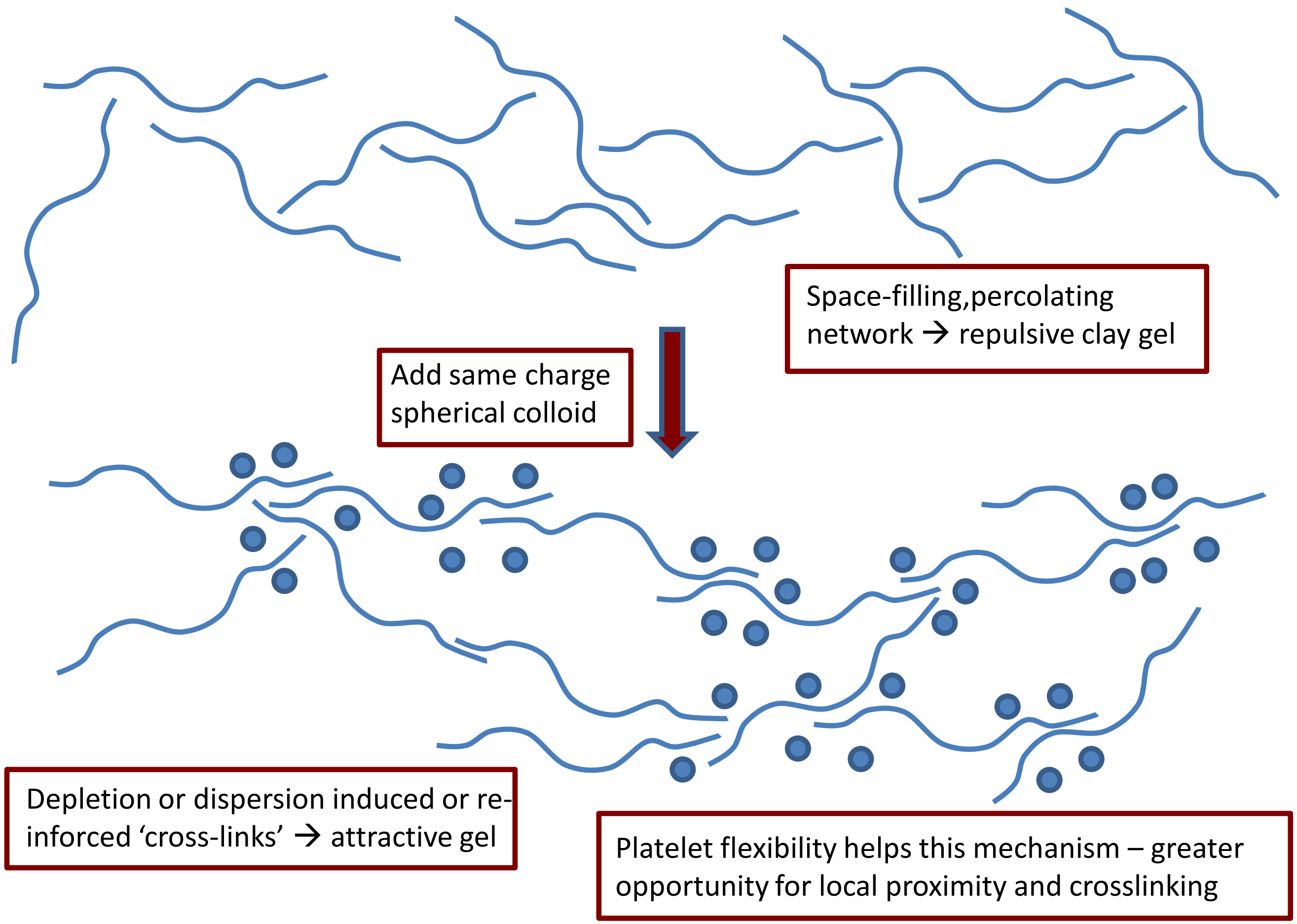
Phase separation with Anionic silica

Diluted suspensions for TEM study ~0.01 wt%



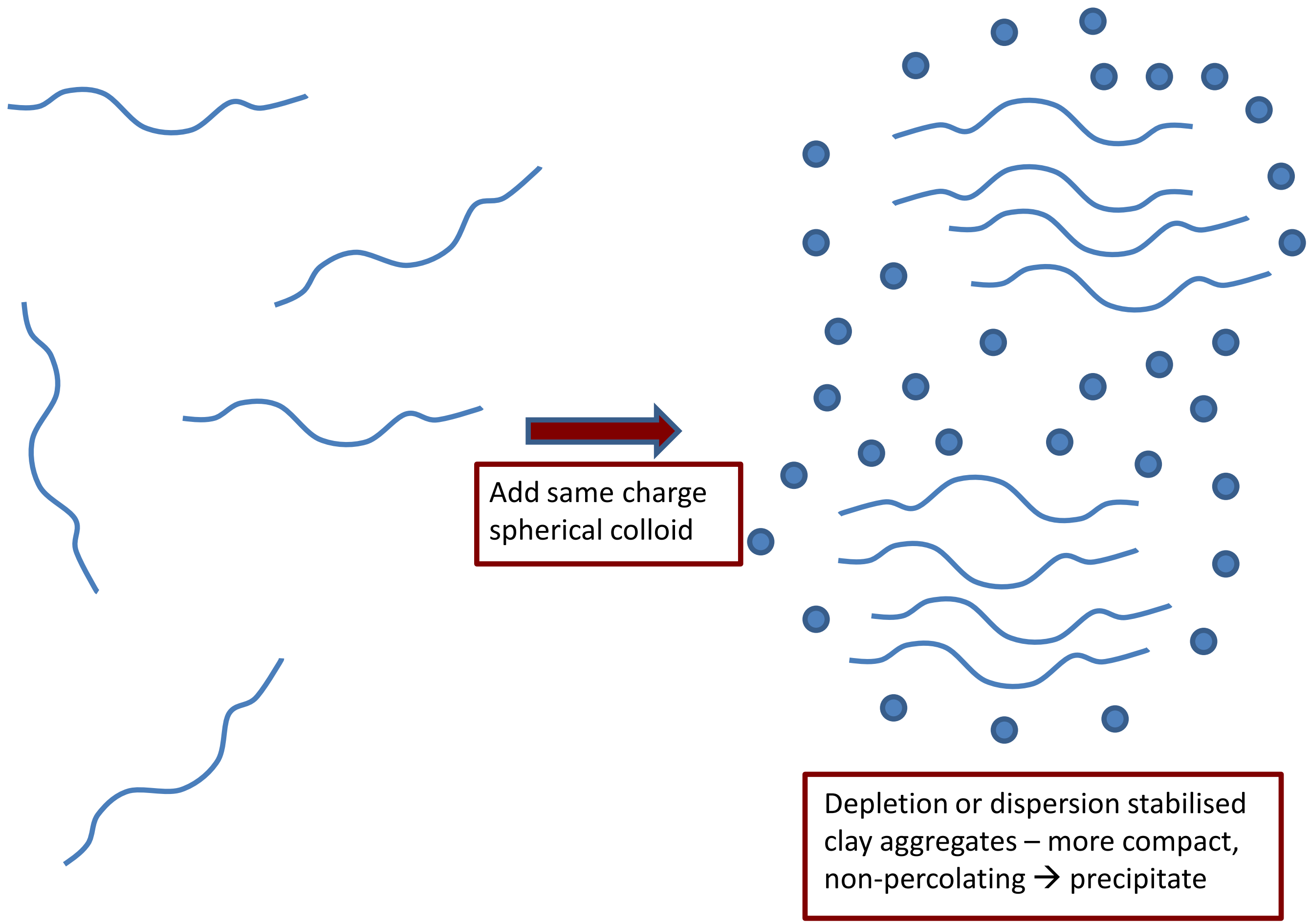
2.4 wt% suspension with AS40 also developed ppt after standing for some time

Anionic Silica addition c > c*



Clay gel hinders bulk phase separation

Anionic Silica addition $c < c^*$



No gel to hinder bulk phase separation

Conclusions

- Montmorillonite & Hectorite rheology, $c \sim c^*$ $c > c^*$ broadly similar
  - Hectorite: stronger gels & a more complex steady shear rheology due to particle stiffness
- Addition of second colloid changes rheology
  - Same trends with sign of charge & size of colloid
  - Cationic: heterflocculation
  - Anionic: dispersion / depletion flocculation

  - $c > c^*$ enhanced gels with both cationic and anionic silica
  - $c < c^*$ cationic silica enhances gel, anionic silica destroys gels

- Clay systems still have occasion to surprise us

Acknowledgments

My coauthors, especially Geoff

Schlumberger Cambridge Research

Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)

SoftComp EU 6th Framework Network of Excellence